



Short communication

Mosaic-shaped cathode for highly durable solid oxide fuel cell under thermal stress



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HIGHLIGHTS

- A novel method for the fabrication of a mosaic-shaped cathode is introduced.
- By adjusting the amount of binder, the mosaic-shaped cathode is successfully achieved.
- The stress at the cathode/electrolyte interface is alleviated by the mosaic structure.
- The mosaic-shape cathode exhibits highly enhanced durability for thermal cycles.

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ABSTRACT

In this study, we propose a novel “mosaic structure” for a SOFC (solid oxide fuel cell) cathode with high thermal expansion to improve the stability against thermal stress. Self-organizing mosaic-shaped cathode has been successfully achieved by controlling the amount of binder in the dip-coating solution. The anode-supported cell with mosaic-shaped cathode shows itself to be highly durable performance for rapid thermal cycles, however, the performance of the cell with a non-mosaic cathode exhibits severe deterioration originated from the delamination at the cathode/electrolyte interface after 7 thermal cycles. The thermal stability of an SOFC cathode can be evidently improved by controlling the surface morphology. In view of the importance of the thermal expansion properties of the cathode, the effects of cathode morphology on the thermal stress stability are discussed.

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1. Introduction

Recently, there has been growing interest in developing high performance cathodes for intermediate temperature solid oxide fuel cells (SOFC). Promising materials are commonly based on the mixed conducting perovskite oxides (ABO_3) containing rare and/or alkaline earth metals on the A-site and transition metals on the B-site [1,2]. Among these, Ba-based cobaltite cathodes have showed remarkably high performance, and have much higher

oxygen reduction activity than the conventionally used lanthanum manganite electrodes at low operating temperatures. Therefore, the use of cobalt-containing cathode materials such as $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) is gaining increased attention [3–6]. Even though promising results have been reported, a large thermal expansion coefficient (TEC), and chemical and structural instability limit applications of these materials [7,8]. Generally, Co-based cathodes have large TEC because the concentration of oxygen vacancies with the reduction of Co ion, considerably increases at elevated temperature. BSCF has quite high TECs (typically larger than $20 \times 10^{-6} \text{ K}^{-1}$), compared to those of electrolytes (about $10\text{--}13 \times 10^{-6} \text{ K}^{-1}$). [9] The TEC mismatch between the cathode and the electrolyte generates thermal stress during both the firing procedure of the cathode layer and the operation of the fuel cell, which lead to delamination at the cathode/electrolyte interface or cracking of the electrolyte.

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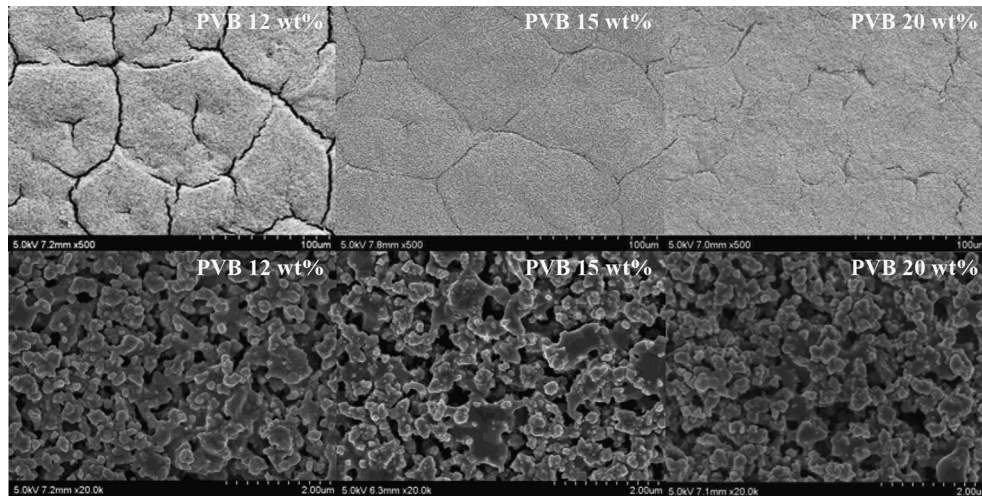


Fig. 1. Surface morphology of the BSCFZ–LSCF cathodes measured by SEM.

Many researchers have reported that the thermal expansion behavior of cathodes can be tailored using either composite cathodes consisting of perovskite and appropriate amount of electrolyte or alternative perovskites doped with different kind of dopants [10–12]. Recently, to inhibit interfacial delamination in various thermal conditions, new concepts of coating design have been introduced, such as duplex, multilayer, gradient, and segmented coating (mosaic-shaped morphology) [13–15]. Even though, so far, the interfacial delamination mechanics for the protective coating

system have been intensively studied, very few studies have been conducted on morphology considerations (coating designs) to enhance the thermal stability of SOFC cathodes. In this study, to improve the stability against thermal stress and, accordingly, the durability of the fuel cell system, we propose a new “mosaic structure” for an SOFC cathode. The purpose of this design is to alleviate the mismatch stress level across the cathode and the electrolyte interface. A similar concept has already been proposed in the patent that a patterned SOFC electrode can reduce the strain

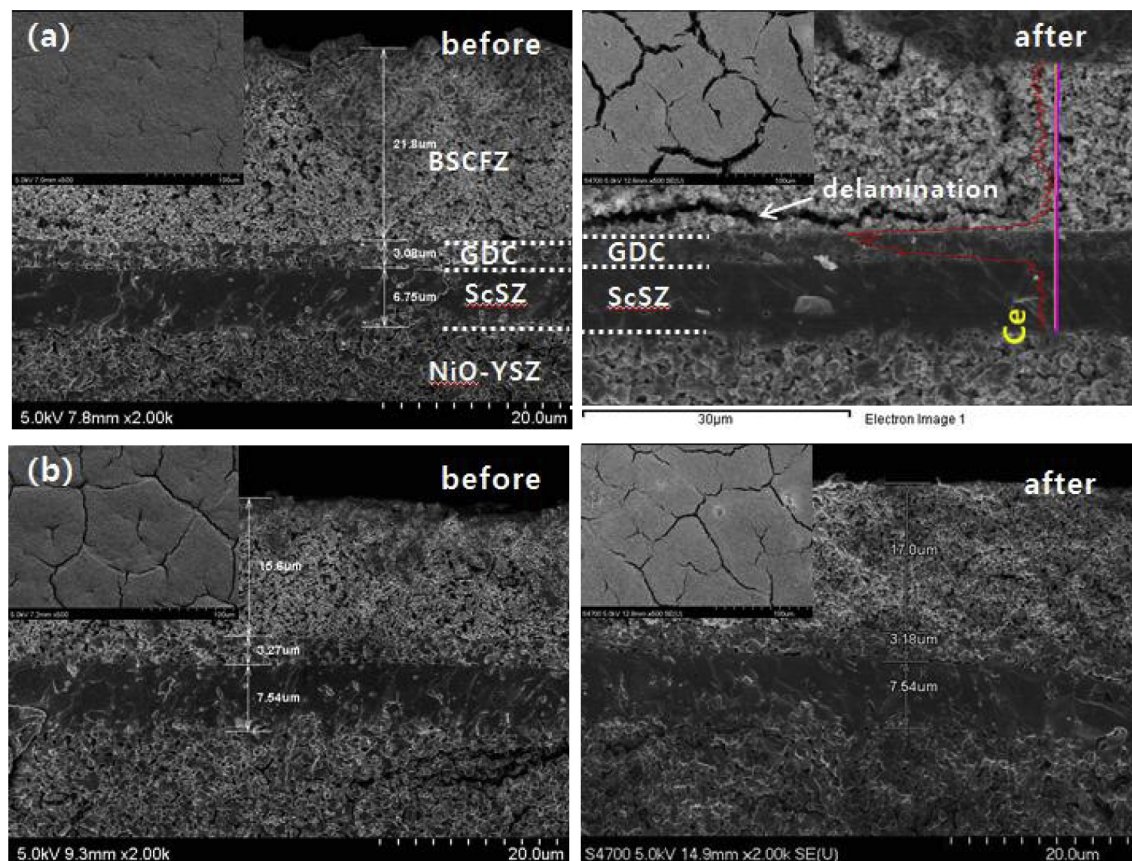


Fig. 2. SEM micrographs of anode-supported consisting of BSCFZ cathode, GDC10 buffer layer, ScSZ electrolyte and NiO/YSZ anode cells before and after thermal cycles. EDX line profile of Ce as a function of distance is also shown. (a) Non-mosaic cathode (20 wt.% PVB) (b) Mosaic cathode (12 wt.% PVB). Inset shows the top view SEM images after thermal cycling.

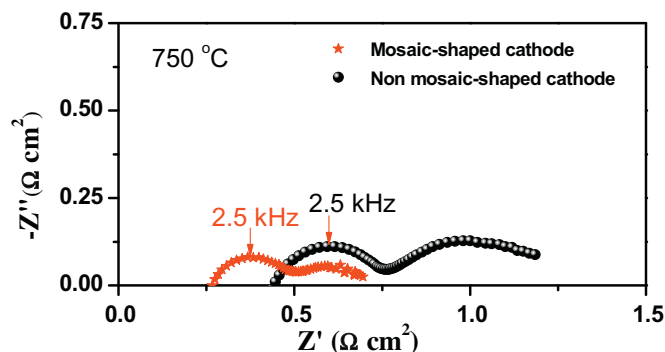


Fig. 3. The impedance spectra of mosaic and non-mosaic cathodes at 750 °C in open circuit condition.

at the interface, thereby reducing delamination and increasing thermal cycling capability, but to the best of our knowledge, this has not been experimentally verified in the field of SOFC research. Therefore, the experimental data is required to validate the predictions [16]. Electrochemical measurements and cycling tests were performed to confirm the thermal stress stability of the mosaic electrode. This electrode was highly durable for rapid thermal cycles. The results prove that controlling the morphology of the cathode can considerably enhance the durability against thermal stress.

2. Experimental

A mixed powder of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.1}\text{Zn}_{0.1}\text{O}_{3-\delta}$ (BSCFZn) and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF6428, Kceracell, Korea) was used as the cathode material in this study. It has been reported that the TEC of BSCFZn ($\sim 17 \times 10^{-6} \text{ K}^{-1}$) is lower than that of BSCF ($\sim 20 \times 10^{-6} \text{ K}^{-1}$) due to the presence of redox-inactive Zn^{2+} in the B site of the perovskite structure [12]. BSZFN was synthesized using a conventional solid state reaction with high purity oxide powders. Stoichiometric amounts of BaCO_3 (99.9%, Sigma–Aldrich), SrCO_3 (99.9%, Sigma–Aldrich), Co_3O_4 (99.9%, CoreMax), Fe_2O_3 (99.9%, Sigma–Aldrich), and ZnO (99.9%, Alfa Aesar), were ball-milled in ethanol for 3 days. The mixed powders were dried, calcined in air at 970 °C for 3 h and at 1030 °C for 10 h, respectively, with intermediate regrinding. The electrochemical performances of the BSCFZn–LSCF cathodes were evaluated with anode-supported single-cell SOFCs. The anodes were prepared by ball-milling of NiO (99.97%, High Purity Chemicals) and 8 mol% yttria doped zirconia (hereinafter “8YSZ”, 99.9%, TZ-8Y, Tosoh) with a volume ratio

of Ni:8YSZ = 45:55 in ethanol for 2 days. The obtained powder mixture was uniaxially pressed (diameter 25.4 mm) at $3.53 \times 10^7 \text{ Pa}$; this was followed by pre-sintering at 1150 °C for 3 h. ScSZ (Scandia-stabilized zirconia, $\text{Zr}_{0.89}\text{Sc}_{0.1}\text{Ce}_{0.01}\text{O}_{1.95}$, DKKK) electrolyte was deposited onto the NiO–YSZ substrate by dip-coating and sample was cured at 1000 °C for 3 h. Afterward, a 10 mol% Gd-doped ceria (GDC10, Anan-Kasei) interlayer was deposited on the ScSZ electrolyte by dip-coating to prevent any reaction between the cathode and the ScSZ. The electrolyte and the GDC interlayer were co-sintered at 1350 °C for 3 h. In order to investigate the effect of the BSCFZn–LSCF cathode morphology on the electrochemical performance, different cathode slurries were prepared by varying the amount of binder (Polyvinylbutyral, PVB) from 12 wt.% to 20 wt.% (expressed in wt.% of the total powder weight) in the dip-coating solution. The slurries of the BSCFZn–LSCF mixture with a weight ratio of 1:1 (52:48 vol.%) were deposited onto a sintered GDC interlayer by dip-coating; sample was then fired at 950 °C for 3 h. According to EDX (La and Ba element map) and X-ray diffractometry (Rigaku 2200) data, LSCF and BSCFZn particles are well-distributed without the formation of secondary phase for all investigated composite cathodes. Thus, the interdiffusion at firing temperature 950 °C between LSCF and BSCFZn is negligible. Pt paste (No. 6926, Engelhard) was brush painted on and sample was subsequently heated at 900 °C for 1 h in air. The SOFC cells were sealed with a silver ring into an alumina tube by holding them at a temperature of 960 °C. To evaluate the durability, the cell was repeatedly heated and cooled between 600 °C and 800 °C at a heating/cooling rate of 10 °C min^{-1} . Hydrogen and synthetic air were used as the fuel to the anode and the oxidant gas to the cathode, respectively, with flow rates of 100 ml min^{-1} . An electrochemical interface (Solartron, SI 1287) and an impedance analyzer (Solartron, SI 1260) were used to obtain the impedance spectra. Current versus cell potential was measured using an electrochemical interface (SI1287). The microstructure of the cells was examined using a scanning-electron-microscope with energy-dispersive X-ray spectroscopy (SEM-EDX, Hitachi, S-4700).

3. Results and discussion

We investigated the morphological changes of the cathodes with the varying of the amount of binder in the dip-coating solution. Fig. 1 shows the influences of different amounts of binder on the surface morphology of the BSCFZn–LSCF composite cathodes. According to the high magnification images, there is negligible difference in the microstructure of the electrodes, however, in the low-magnification micrographs, it is evident that the surface

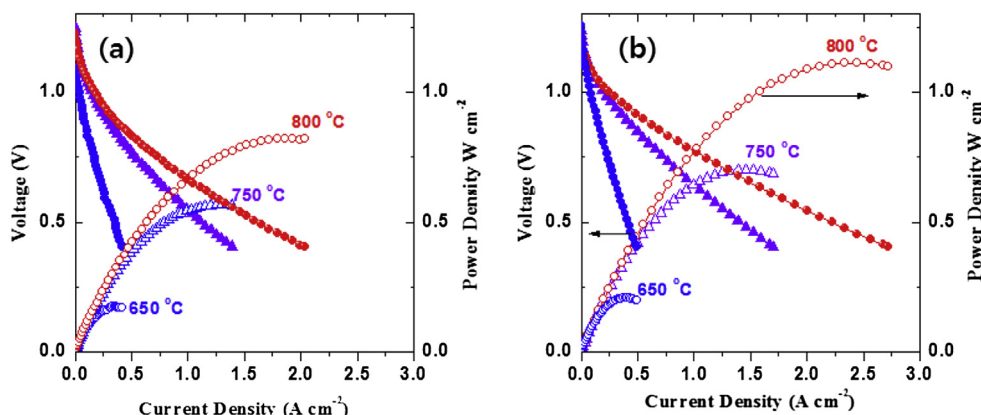


Fig. 4. Current–voltage and current–power curves of the cells with non-mosaic (a) and mosaic (b) cathodes at 650, 750, and 800 °C.

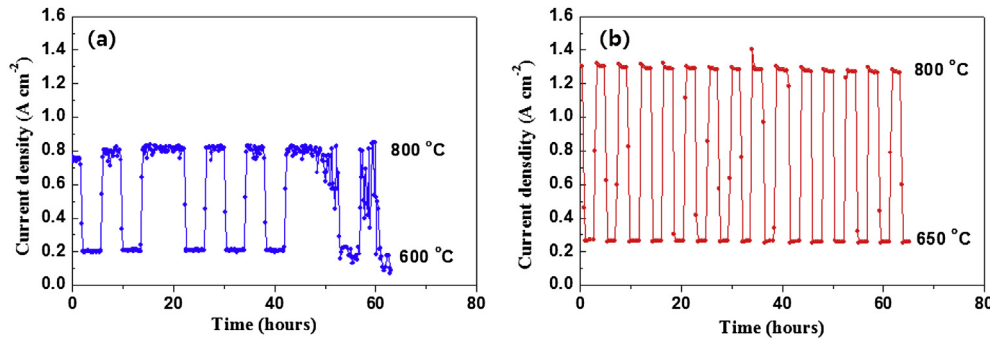


Fig. 5. The current density at 0.7 V of the cells with non-mosaic (a) and mosaic (b) cathodes as a function of thermal cycles between 600 °C and 800 °C with heating and cooling rate of 10 °C min⁻¹.

morphology depends strongly on the amount of binder. Irregular mosaic-shaped domains were found to develop when there was a low amount of binder (PVB 12 wt.%), while the mosaic shape disappeared with an increase of the amount of binder. Under a condition of relatively low amount of binder, the mosaic-shaped electrode is preferred; this is perhaps due to the low binder content, which is insufficient to be dispersed through all the particles in the electrode. The amount of binder is one of the crucial factors for determining the surface morphology of electrodes deposited by slurry coating. It should be noted that self-organizing mosaic-shaped cathode was successfully achieved by controlling the amount of binder in the solution.

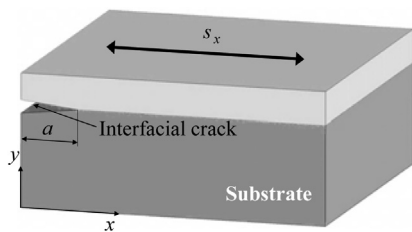
To evaluate the stability of the mosaic-shaped cathode (binder content: PVB 12 wt.%) under thermal stress, thermal cycling tests were performed in ambient air. For comparison, the non-mosaic cathode (binder content: PVB 20 wt.%) was also tested. The cells were repeatedly heated and cooled between 400 °C and 800 °C at a rate of 10 °C min⁻¹. Fig. 2 provides cross-sectional SEM micrographs of the cells before and after five thermal cycles. Before the cycling test, good adhesion between the cathode and the electrolyte was shown for both the mosaic and the non-mosaic cathodes, however, the non-mosaic cathode layer was delaminated from the electrolyte and the propagation of surface crack was also observed after 5

thermal cycles. EDX line profile of Ce as a function of distance is also shown to evaluate the place where the delamination occurs. As shown in Fig. 2(a), the delamination occurred at the GDC/cathode interface. On the other hand, good adhesion at the interface between the cathode and the electrolyte was clearly confirmed after thermal cycles in the mosaic cathode. Further crack propagation at the surface was also negligible. This proves that mosaic-shaped cathode is much more durable than non-mosaic cathode for thermal cycles.

In order to confirm the effects of cathode surface morphology on the electrochemical characteristics of the SOFC cells, the impedance of cells under open-circuit conditions was measured, with results as shown in Fig. 3. A fuel gas of H₂ was fed to the anode; synthetic air was used as the oxidant. The cell with a non-mosaic cathode showed larger ohmic and polarization resistances compared to those with the mosaic cathode. The cell was heated to 960 °C, the melting point of the Ag sealant, before the cell performance measurement. During the heating procedure, adhesion between the cathode and the electrolyte may deteriorate due to the large TEC mismatch. Gazzarri et al. reported changes of impedance spectra due to electrode delamination in solid oxide fuel cells [17]. According to their simulation, which used finite element models, both of high-frequency intercept with the real axis (ohmic resistance) and the diameter of the impedance arc (polarization resistance) increase with the increase of the delaminated area. The increased ohmic resistance indicates an increase in the series resistance due to the decrease of the ionic conduction area, which decrease is induced by the delamination. The increase in the diameter of the impedance arc can be explained by the decrease of the number of available reaction sites, which is caused by the delamination. Our results for the impedance spectra of the SOFC with mosaic- and non-mosaic-shaped cathodes, shown in Fig. 3, are consistent with the reported modeling results for delamination [16]. Thus, relatively large ohmic and polarization resistances in the cell with the non-mosaic cathode can be explained by delamination.

To evaluate the effects of rapid thermal cycling (heating and cooling rate of 10 °C min⁻¹) on the electrochemical performance, the cells with the two different types of cathode were cycled between 650 °C and 800 °C while recording the current densities at 0.7 V. The maximum power densities of the cells with the mosaic and of the non-mosaic cathode were 1.11 W cm⁻² and 0.69 W cm⁻², respectively, at 800 °C (Fig. 4). The low maximum power density of the latter cell resulted from the high ohmic and polarization resistances, as presented in Fig. 3. As the thermal cycles progressed, the performance of the cell with the non-mosaic cathode deteriorated. After 7 thermal cycles, the current values at 0.7 V were found to be significantly degraded as shown in Fig. 5(a). The scattered signals from the sixth cycling measurement indicate that the contact between the cathode and the electrolyte became poor because

(a) Un-segmented coating layer



(b) Segmented coating layer

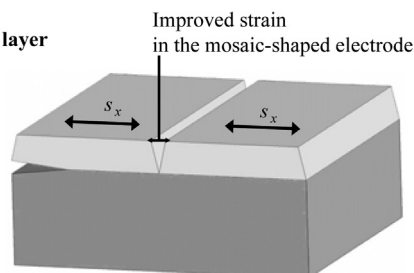


Fig. 6. Improved strain tolerance in the mosaic-shaped electrode (s_x : stress in x direction and a : initial crack length).

crack propagation was initiated. Further measurement was impossible due to the failure of the cell after 7 thermal cycles. On the other hand, very limited deterioration was observed in the cell with the mosaic cathode. This cell showed very stable performance during 15 thermal cycles, as shown in Fig. 5(b). The results also demonstrate that the mosaic cathode remarkably improved the endurance against thermal cycling by reducing the stress at the interface.

A coating layer with a TEC higher than that of the substrate is inevitably exposed to tensile residual stress during cooling procedures. If the thermal shock or the fatigue is severe enough, interfacial delamination occurs to release the mechanical stress. Promising cathode materials with single or double perovskite structures are easily delaminated from electrolytes such as GDC and YSZ during thermal cycling tests due to the great differences in TEC [18,19]. Since the TEC values of BSCFZn and LSCF are $\sim 17 \times 10^{-6} \text{ K}^{-1}$ [12] and $\sim 16 \times 10^{-6} \text{ K}^{-1}$ [20], respectively, the TEC of BSCFZn–LSCF composite is reasonably assumed between 16 and $17 \times 10^{-6} \text{ K}^{-1}$. Despite such a large TEC difference, however, the cathode with the mosaic structure (12 wt.% PVB) showed a highly durable performance in the fluctuating thermal environment.

The mosaic-shaped electrode has a coating layer with periodic segmented cracks moving toward the interface with penetration depths comparable of the layer thickness, as shown in Fig. 6. Because its TEC value is larger than that of the electrolyte, the cathode layer is exposed to tensile residual stress during cooling conditions. This surface stress can initiate surface crack propagation, which leads to delamination. However, it has been reported that pre-existing segmented cracks (of mosaic shape) in the cathode significantly decrease the surface tensile stress as segmented crack density increases. Since the mosaic cathode has periodic segmented cracks that allow the strain at the interface to be released under tensile and compressive stress, the strain tolerance of the coating layer is improved and the macroscopic stiffness decreases [21–23]. Thus, the interfacial delamination problem can be alleviated. This theory in the field of interfacial delamination mechanics strongly supports the idea that a mosaic cathode can endure more strain mismatch during thermal cycling.

4. Conclusions

By adjusting the amount of binder, a mosaic-shaped cathode has been successfully fabricated using the dip-coating method. The self-organizing mosaic-shaped structure alleviates the stress due to the TEC mismatch across the cathode/electrolyte interface. The performance of a cell with a non-mosaic cathode has been found to be severely deteriorated during rapid thermal cycles due

to delamination at the interface, while the cell with the mosaic cathode shows very stable performance. This cathode layer with mosaic morphology shows dramatically enhanced durability in a fluctuating thermal environment. This investigation demonstrates that controlling the morphology of the cathode is a decisive role for improving the durability against the thermal stress. This feature could be useful for the designing of thermal shock resistant electrodes in SOFC.

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